Armed Services Technical Information Agency

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FINAL REPORT

on

Contract Number ONR 222-02

Project Number NR 051-266

"Rates of Chemical Reactions in Homogeneous

Liquid Solutions".

By

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August   1954   Berkeley, California

Two general approaches to a problem are in general use. The first considers a relatively large number of systems and draws general conclusions. The data for any one system usually are only qualitative. Frequently the systems being compared are not under identical conditions. Deviations from conclusions are brushed away as "experimental errors."

The second considers a very limited field - one or two systems - and attempts to explore these systems not only in detail but with precision. The work is slow but discrepancies between experiment and theory mean that the theory must be revised. The second method is the auditor of the results of the first method. This method was the core of the original proposal for this project.

Two reactions were selected for study: (1) The racemization of l-bromo succinic acid by lithium bromide in aqueous acetone solution, and (2) The solvolysis of t-butyl halides in aqueous organic solvents.

The ionization of lithium bromide in aqueous acetone solution was determined by J. Konecny.[1] Reprints have been circulated.

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1. A. R. Olson and J. Konecny, J.A.C.S., __75__ 5801 (1953).

Using these results it was found that the rate of racemization of the l-dimethyl ester of bromo succinic acid by lithium bromide in acetone solution could be explained fairly well by introducing the conventional Debye Hückel salt effects. Olson, Frashier and Spieth[2]

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2. A. R. Olson, L. D. Frashier and Frances Spieth, Journal of Physical and Colloidal Chemistry, __55__, 860 (1951).

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had assumed specific interactions to account for the rate. It
so far has not been possible to account for the rate of racemization
of l-bromo succinic acid by lithium bromide by the conventional
theory. Here the interactions are very much larger than they are
for the ester. This work was supported only during a short summer
period and was interrupted when Mr. Konecny received his degree.

The study of the solvolysis of the t-butyl halides is deline-
ated in a series of articles. The composite rate of solvolysis
of t-butyl chloride in aqueous methanol, aqueous acetone and aqueous
dioxane, and of t-butyl bromide in aqueous acetone, have been de-
termined at several temperatures. Empirical equations which repre-
sent these rates to about 1% have been derived. The material is
presented and discussed in a manuscript which has been accepted by
J.A.C.S. for publication under the title "The Specific Rates of
Solvolysis of t-butyl Chloride" etc.

The Solvolysis of t-Butyl Chloride in Aqueous Methanol
yields the products isobutene, methyl t-butyl ether and t-butanol.
The percentages of these products depend upon the solvent compo-
sition and to some degree on the temperatures. A method has been
devised to analyze for these products with a precision of about 1%.
The method and results are presented in an article which has been
accepted for publication by the J.A.C.S.

One of the factors that originally was proposed by Olson and
Halford, and which has since been adopted by others to explain the
rate of solvolysis of these substances is the Henry's Law Constant
of the tertiary halides. The determination of this constant at
various solvent compositions has presented some difficulties.
These have been overcome. The methods and results are summarized
in a note to the J.A.C.S. which has been accepted for publication.

One of the important results of this investigation was the discovery of the large increase in the partial molal heat content of butyl chloride as N_w increases. This absorption of heat occurs immediately on dissolving -- the reaction of butyl chloride with the solvent is a slow follow process which occurs hours or days later. Use has been made of these phenomena to elucidate the reaction mechanism.

The partial pressures of water and methanol occur in the rate expressions that have been proposed for the solvolysis reaction. We have derived an expression for the activity of methanol in these solutions at the temperature at which the pressures were measured. By the Duhem equation we have calculated the activity and partial pressure of water at 25°C. The results are collected in a note that has been sent to the J.A.C.S.

From the partial pressures and the product compositions the rate equations that have been proposed by various investigators have been tested. In an article submitted to the J.A.C.S. it is shown that none of the published equations fits the data. Two sets of equations, one involving the partial pressures and one involving only mole fractions, are derived, which give the correct ratios

$\dfrac{\text{Isobutene}}{\text{Ether}}$ and $\dfrac{\text{Ether}}{\text{Butanol.}}$ Each of these equations must be multiplied by a factor F in order to give the observed rate. Log F is found to be of the form $a + b\, N_w$, where a changes with the temperature. From the studies on the Henry's Law Constant it can be shown that b also must change slightly with the temperatures, and that therefore the empirical rate equations must be adjusted (within the assumed error limits). This leads to the following conclusions:

1. Butyl chloride absorbs a large amount of heat on dissolving
in aqueous methanol. The heat increases as the water content of
the solvent increases. The effect may be due to a real hydration
of the butyl chloride or to a dielectric constant change The
carbon chlorine bond seems to be weakened, resulting in a decrease
of energy of activation when the molecules react. Pulling the
chlorine further away from the central carbon permits an increase
in the angle between the methyl groups. This in turn decreases the
steric hindrance and therefore increases the entropy of the reaction
as N_w increases.

2. The heat of solution is small compared to the heat of acti-
vation. At $N_w = .5$ it is only from ten to fifteen per cent of ΔE.
This is in accord with the fact that reaction is a slow step
which may be separated from solution by hours or days.

The form of the equations corresponds to:

a) A bimolecular reaction between butyl chloride and water to
form butanol.

b) A bimolecular reaction between butyl chloride and methanol to
form ether, and

c) An elimination of hydrochloric acid to form isobutene.

We find no necessity for introducing carbonium ions to explain
the reactions. These solvent effects cannot be considered a dis-
tinguishing criterion for the mechanism of primary ionization.

The salt effects on the rate of solvolysis of t-BuCl and t-BuBr
in aqueous acetone have been studied and the results have been
collected in a manuscript which is being submitted to the J.A.C.S.
for publication. Here it is shown that $\log \Delta K = \alpha + \beta N_w$ where

ΔK is $k_{salt} - k^\circ$. The fact that the weakest salts have the largest effects makes it difficult to explain in terms of conventional Debye-Hückel salt effects. The effects, however, may be in the same order as the salt effects on the partial molal heats contents of the butyl halides. Thus the salts and water play analogous roles.

Reprints of the above articles will be available on request to the Department of Chemistry of the University of California, Berkeley, California.

Finally, I wish to express my gratitude to the Office of Naval Research for their support, and for the complete freedom of action that has been accorded me.

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